
Molecular Mechanics (MM4) Calculations on Alkenes*

NEYSA NEVINS, KUOHSIANG CHEN, and NORMAN L. ALLINGER[†]

Computational Center for Molecular Structure and Design, Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556

Received 25 March 1995; accepted 29 September 1995

ABSTRACT

The MM4 force field has been extended to alkenes. It retains most of the formalism and computational schemes that were present in MM3. Several additional cross-terms have been added in MM4 that were not present in MM3, mainly to improve vibrational frequencies but also to improve structures and energies. About 100 molecules have been examined, many in multiple conformations. Geometries are fit for the most part to within the following ranges: 0.004 Å for bond lengths, 1° for bond angles, 4° for torsion angles, and 0.5% for moments of inertia (r_z). Conformational energy differences/barriers are generally fit to within 0.5 kcal/mol unless they are very large. The vibrational frequency rms error for 7 alkenes is 25 cm⁻¹. © 1996 by John Wiley & Sons, Inc.

Introduction

There were several problems with the MM3 force field¹ that became apparent only after it was in use for some time. The most obvious problem was that spectroscopic frequencies were not very well calculated. For a standard set of saturated hydrocarbons,^{1b} the root mean square (rms)

error in the frequencies was 36 cm⁻¹. When the MM3 force fields for alkenes² and conjugated hydrocarbons³ were later developed, we were disappointed to find that the rms errors for standard sets of each of these two classes of compounds[‡] were, respectively, 41 and 56 cm⁻¹. The major single source of error leading to these rather large rms errors was the omission of a bend-torsion-bend

*This article includes Supplementary Material available from the authors upon request.

[†] Author to whom all correspondence should be addressed.

[‡] The apparent errors were initially better than this, in part because a small set of compounds was used and in part because of a serious experimental misassignment of one of the frequencies of benzene. When the larger set of compounds studied herein was used and the frequencies were all correctly assigned (according to our current knowledge and beliefs), the results were as stated (see later).

interaction term. It was known from the work of Snyder and Schachtschneider⁴ as long ago as the 1960s that this term was rather important for the calculation of vibrational spectra, but it had been omitted in MM3. In MM4 this term was added,⁵ and other small changes were made, and the rms error of the standard set of alkanes was reduced from 36 cm⁻¹ to 24 cm⁻¹. This improvement is more significant than it may at first appear, because it is not that many frequencies were slightly improved, but rather that a few frequencies were greatly improved. These frequencies involve mainly hydrogen bendings, and they occur around 1000 cm⁻¹ in the vibrational spectrum. They do not have any significant effect on the geometries of alkanes that we have been able to ascertain, and they are too high to affect properties such as entropy. So, in fact, they do not seem to be very important in the real world. It is nonetheless worthwhile to reduce these errors, because a force field is constructed in such a way that an error any place will lead to other errors in an effort to compensate for the first error, and a propagation of these errors may lead to unexpected problems.

As MM3 was further developed and applied to functionalized molecules,⁶ it turned out that these same bend-torsion-bend interactions were consistently important. The errors tended to be larger in planar systems, and there tended to be more frequencies (both in-plane and out-of-plane) that were affected. The required cross-term in the force field changes the splitting between different related frequencies that are coupled together. By adjusting the bending force parameters properly, one can calculate the average of the frequencies reasonably well. However, one cannot calculate the individual frequencies correctly (by 100 cm⁻¹ or so) unless one explicitly includes these cross-terms. As with the alkanes, as far as we could determine, there was no effect on structure, and little effect on anything else, from these frequency errors.

The initial major thrust for the MM3 to MM4 improvement was the addition of these bend-torsion-bend cross-terms and the better optimization of the vibrational frequencies. Once this error had been much reduced, other errors could be more realistically examined. There were several of these, and they will be detailed later. They all have various modest but significant effects on the overall results of the force field.

The MM3 force field already does a fairly good job of treating alkenes and conjugated hydrocar-

bons.^{2,3} The major changes that are present in MM4, relative to MM3, will first be briefly outlined here for alkenes. They will subsequently be taken up one by one. Some discussion of conjugated molecules will be given here, but as a whole they are deferred to the following articles.

In addition to the bend-torsion-bend interaction mentioned above, there were several other spectroscopic problems. One of these was the stretch-stretch interaction between partial double bonds in conjugated molecules such as benzene. The notorious B_{2u} frequency in benzene (see footnote ‡ on previous page) was fit incorrectly with MM3, because what we regarded as the best interpretation of the available data at the time that MM3 was formulated was subsequently changed (mainly on the basis of *ab initio* calculations), and that frequency was lowered about 300 cm⁻¹. Hence while MM3 fit the original frequency adequately, when we look at the correct frequencies (as we now know them), there is a very large error in this one frequency and thus in the rms fit of the frequencies. The *ab initio* frequency was fit with MM4.

A second important point is mainly geometric. As ethylene rotates over the high barrier about the double bond, the MM3 molecule pyramidalizes at both carbons, so that the transition state does not have simple D₂ symmetry but is highly distorted. The MM3 energy barrier calculated is also much too low, 35.6 vs. 65 kcal/mol experimentally. One can use a larger V₂ torsional constant or a torsion out-of-plane bending-type cross-term to raise this barrier. Both were used in MM4. However, either of these modifications has an adverse effect on various other things, so that the rotational barrier in ethylene was compromised and is still calculated too low with MM4 (50.7 kcal/mol), although it is much improved over that calculated with MM3.

Another important structural problem concerns the small bridged *In*-cyclophanes. In these molecules there is a close approach of a hydrogen to the face of an aromatic ring. The distance of approach was too large (+0.12 Å) in the MM3 calculations, but with MM4 it is closer (+0.02 Å) to the experimental value. Conjugated hydrocarbons are, on the whole, much more complicated and difficult to deal with in a force field than are alkenes. The improvements in the structures and energies of these compounds are many, and significant, and they will be detailed in two following articles.⁷

Molecular Mechanics

The MM4 molecular mechanics force field⁸ is outlined in this section. The force field begins with the same equations utilized in the MM3 program,¹⁻³ and those will not be discussed here. The new MM4 equations (cross-terms) were added to those which previously were used in MM3, and one type of term was modified.[‡] The MM4 force field is defined in general terms by eqs. (1)–(4).

$$E_{\text{MM4}} = \sum E_{\text{retained MM3 terms}} + \sum E_{\text{new MM4 terms}} + \sum E_{\text{modified MM3 terms}} \quad (1)$$

$$E_{\text{retained MM3 terms}} = \sum (E_{\text{str}} + E_{\text{bend}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{dipole}} + E_{\text{bend-bend (one-center)}} + E_{\text{str-bend}}) \quad (2)$$

$$E_{\text{new MM4 terms}} = \sum (E_{\text{str-str}} + E_{\text{tors-bend}} + E_{\text{bend-tors-bend}} + E_{\text{tors-tors}} + E_{\text{tors-impt}} + E_{\text{impt-tors-impt}}) \quad (3)$$

$$E_{\text{modified MM3 terms}} = \sum (E_{\text{impt}} + E_{\text{tors-str}}) \quad (4)$$

We have made one formal change from the MM3 force field. In MM3, we used out-of-plane bending as a way to describe that kind of motion. In MM4, we have reformulated this as an improper torsion, because the programming is far simpler with the latter formulation, and parallel calculations by both methods show that the difference between the two methods is insignificant.

Stretching and bending were treated as previously. Torsion was treated as previously, with one change. Originally, force fields assumed that saturated molecules had a V_3 potential, and unsaturated molecules had a V_2 potential. Later it was shown that one really needs to use V_1 , V_2 , and V_3 to reproduce adequately torsional potentials of molecules in a general way.⁸ For alkanes, a small V_6 potential for $\text{H}-\text{C}-\text{C}-\text{H}$ allows one to calculate torsional frequencies and energy barriers simultaneously slightly better than if this term is not included.⁵ Similarly, a V_4 term allows one to

calculate both the torsional frequencies and the rotational barrier better in a molecule like ethylene than if this term is not included. This was noted long ago,⁹ and it was independently found experimentally¹⁰ that such a V_4 term in the potential is needed to describe the higher-level (excited) torsional frequencies for ethylene. This kind of term is also included in MM4.

IMPLICIT OFF-DIAGONAL TERMS

MM4, like MM3, takes all bonds to be nonpolar in alkanes, so that the nonbonded forces consist exclusively of van der Waals types. The same equation is used as previously, although the parameters have been adjusted slightly. For an alkene, there are bond moments between saturated and unsaturated carbons and between hydrogens and unsaturated carbons (similar to those used for MM3). In MM3 and earlier force fields, it was found desirable to use somewhat different van der Waals parameters for a carbon atom, depending on whether the carbon was saturated or unsaturated. Logically, if the saturated and unsaturated carbons are different, then the hydrogens attached to unsaturated or saturated carbons should also be different, although they were taken to be the same in MM3. In MM4, however, they are taken to be different, and their parameters are optimized separately. This permits us to fit a much wider variety of data than could be fit if a single set of parameters were imposed on all hydrogens attached to carbon. Charge-charge, charge-dipole, and dipole-dipole interactions^{11,12} are also included in these terms in MM4, as they were in MM3.¹

EXPLICIT OFF-DIAGONAL TERMS

In MM3, stretch-bend, torsion-stretch, and bend-bend (one-center) interaction terms were present, and those are retained in MM4. Several new terms were added, as discussed later. The new terms include bend-torsion-bend (btb) as described for alkanes,⁵ improper torsion (impt, which replaces the out-of-plane bending in MM3), improper torsion-torsion-improper torsion (ittit), and stretch-stretch (ss), all of which primarily improve the frequency calculations. Also, a torsion-bend (tb) term mainly improves structures, especially bond angles and the resulting moments of inertia, while torsion-improper torsion (timpt) affects ethylene-type barriers. A torsion-torsion (tt) term not only increases coupled out-of-plane bend-

⁸ Bond lengths are in Å, angles are in degrees, and energies are in kcal/mol, except for "spectroscopic constants," where stretching is in mdyne/Å, and bending is in mdyne/rad², and torsion is kcal/mol. The off-diagonal units obtained by multiplying 2 or more of the above have units corresponding to such multiplication unless otherwise stated.

[‡] E_{impt} in MM4 replaces E_{opb} (opb = out-of-plane bend) in MM3. The two give essentially identical results, but the latter is far more complicated to program. Definitions are given in the text.

ing frequencies in conjugated systems, but also affects their energies. This term stabilizes—that is, lowers the energies of—molecules that are more aromatic (i.e., have nearly equal bond orders) relative to those compounds which are less conjugated (alternating high/low bond orders, as in a polyene). A description of the terms is presented next, and the parameter values are listed in Tables IA through IH. The ramifications of these terms will be subsequently discussed further.

Atom types are defined as follows: type 1 (C_{sp^3}), type 2 (C_{sp^2}), type 5 (H attached to C_{sp^3}), type 112 (H attached to C_{sp^2}), type 122 (C_{sp^2} in a five-membered ring), and type 123 (C_{sp^3} in a five-membered ring).

Bend-Torsion-Bend (btb)

The bend-torsion-bend term [eq. (5) and Fig. 1] improves the C_{sp^2} —H in-plane bending frequencies, especially the ethylene B_{1g} and B_{2u} CH_2 rocking frequencies. K_{btb} is the btb parameter, ω is the dihedral angle $A-B-C-D$, and $\theta_{1,2}$ and $\theta_{1,2}^\circ$ are the actual and natural bond angles, respectively. (A discussion of the vibrational frequencies of alkenes will be deferred to a later manuscript.^{7b})

$$E_{btb} = 0.043828 * K_{btb} * \cos \omega * \Delta \theta_1 * \Delta \theta_2$$

$$(\Delta \theta_1 = \theta_1 - \theta_1^\circ, \Delta \theta_2 = \theta_2 - \theta_2^\circ) \quad (5)$$

TABLE IA.
Torsional V1, V2, V3, V4 (kcal / mol), and Bend-Torsion-Bend (BTB) Parameters.^{a,b}

				V1	V2	V3	V4 ^c	BTB
	1	1	1	2	0.00	-0.10	0.85	
	1	1	2	1	0.00	0.00	0.50	
	1	1	2	2	-0.50	0.50	0.20	
	1	1	2	112	-0.20	-0.15	0.85	
	2	1	1	2	0.00	0.00	0.80	
	2	1	1	5	0.00	0.00	0.80	
	2	1	2	2	0.50	-0.15	0.00	
	2	1	2	112	0.50	0.00	-0.20	
	5	1	2	2	0.00	0.00	-0.26	-0.08
	122	122	123	5	0.00	0.00	-0.26	
	5	1	2	112	0.00	0.00	0.40	-0.08
	112	122	123	5	0.00	0.00	0.40	
	5	1	2	1	0.00	0.00	0.50	-0.08
	1	2	2	1	-0.20	16.00	0.00	
	1	2	2	2	-0.50	8.50	-0.50	-0.04
	1	2	2	112	0.20	16.00	0.00	-0.04
	2	2	2	2	-0.20	14.50	0.00	-0.04
	2	2	2	112	0.00	14.50	-0.50	-0.04
	112	122	122	122	0.00	14.50	-0.50	
	112	2	2	112	0.00	16.00	0.00	-0.04
	112	122	122	112	0.00	16.00	0.00	
5	122	122	122	122	0.00	16.00	-1.55	
5	122	122	122	123	-0.80	16.00	0.00	
5	122	122	123	122	0.00	0.00	0.00	
5	123	122	122	123	0.00	16.00	0.00	
5	122	122	123	123	-0.65	-0.80	-0.25	
5	123	122	123	123	0.50	0.00	0.00	
5	122	123	123	123	0.00	-0.80	-0.25	

^a The number 5 in the first column indicates the parameter is contained within a five-membered ring.

^b Note that unless they are given explicitly in the table, parameters involving five-membered ring atom types (122 and 123) are assigned parameters which involve the regular atom types (types 2 and 1). This is true for all parameters.

^c For C_{sp^2} — C_{sp^2} dihedral angles, a V4 term has been included which is -9% (if the double bond is nonconjugated) and -6% (conjugated) of V2 (see conformational analysis section).

TABLE IB.
Bond Length and Dipole Parameters.^{a,b}

			K_s (mdyne / Å)	l_0 (Å)	Dipole (D)	t-Slope	s-Slope
	1	2	5.10	1.501	0.95		
	2	2 ^c	9.30	1.333		4.82	0.170
	2	112	5.15	1.103	-0.60		
	112	122	5.08	1.103	0.60		
5	122	122	8.80	1.336		4.62	0.162
5	122	123	4.20	1.508	-0.95		

^a The number 5 in the first column indicates the parameter is contained within a five-membered ring.^b Note that unless they are given explicitly in the table, parameters involving five-membered ring atom types (122 and 123) are assigned parameters which involve the regular atom types (types 2 and 1).^c An electronegativity correction of +0.002 Å is applied to a type 2—2 bond when a type 1 atom is attached to a type 2 atom.**TABLE IC.**
Bond Angle Parameters.^{a,b}

	Angle			K_b (mdyne Å / rad ²)	θ_0 (°)	Type ^c
	1	1	2	0.52	112.0	2
	1	1	2	0.52	111.7	3
	2	1	2	0.75	113.4	2
	2	1	2	0.75	112.0	3
	2	1	5	0.64	110.4	3
	1	2	1	0.62	117.6	
	1	2	2	0.38	125.0	1
	1	2	2	0.68	123.7	2
	1	2	112	0.45	117.0	
	2	2	2	0.74	122.7	1
	2	2	2	0.74	122.5	2
	2	2	112	0.46	120.0	1
	2	2	112	0.46	120.7	2
	112	2	112	0.47	119.0	
	112	122	122	0.52	120.0	
	112	122	123	0.50	117.5	
	5	123	112	0.52	109.5	
5	122	122	122	0.90	118.0	1
5	122	122	122	0.90	117.6	2
5	122	122	123	0.57	122.6	1
5	122	122	123	0.57	119.2	2
5	122	123	123	0.50	113.2	2
5	122	123	123	0.50	112.7	3
5	122	123	122	0.98	109.0	3

^a The number 5 in the first column indicates the parameter is contained within a five-membered ring.^b Note that unless they are given explicitly in the table, parameters involving five-membered ring atom types (122 and 123) are assigned parameters which involve the regular atom types (types 2 and 1).^c Types 1, 2, and 3 apply when the central atom is substituted, respectively, as —CR₂—, —CHR—, and —CH₂—, apart from the end atoms that define the angle.

TABLE ID.
Torsion-Bend (TB) Parameters.

	$K(\text{tb1})$	$K(\text{tb2})$	$K(\text{tb3})$	$K'(\text{tb1})$	$K'(\text{tb2})$	$K'(\text{tb3})$
1- 1- 1- 2	0.000	0.000	0.000	0.002	0.000	0.000
2- 1- 1- 2	0.002	0.000	0.000	0.002	0.000	0.000
1- 1- 2- 1	0.002	0.000	0.000	0.000	0.000	0.000
1- 1- 2- 2	0.002	0.000	0.000	0.006	0.000	0.000
2- 1- 2- 2	0.006	0.000	0.000	0.006	0.000	0.000
1- 2- 2- 1	0.006	0.000	0.000	0.006	0.000	0.000
1- 2- 2- 2	0.006	0.000	0.000	0.006	0.000	0.000
2- 2- 2- 2	0.006	0.000	0.000	0.006	0.000	0.000
122-123-123-122	0.002	0.000	0.000	0.002	0.000	0.000
1-122-123-122	0.002	0.000	0.000	0.000	0.000	0.000
2-122-123-122	0.002	0.000	0.000	0.006	0.000	0.000
122-122-123- 1	0.002	0.000	0.000	0.006	0.000	0.000
122-122-123-123	0.002	0.000	0.000	0.006	0.000	0.000
1-122-122-123	0.006	0.000	0.000	0.006	0.000	0.000
1- 2-122-123	0.006	0.000	0.000	0.006	0.000	0.000
1-123-123-122	0.000	0.000	0.000	0.002	0.000	0.000
122-123-123-123	0.000	0.000	0.000	0.002	0.000	0.000
122-122-123-122	0.006	0.000	0.000	0.006	0.000	0.000
2-122-123-122	0.006	0.000	0.000	0.006	0.000	0.000
2- 2- 2-122	0.006	0.000	0.000	0.006	0.000	0.000
2- 2-122-122	0.006	0.000	0.000	0.006	0.000	0.000
2-122-122-122	0.006	0.000	0.000	0.006	0.000	0.000
122-122-122-122	0.006	0.000	0.000	0.006	0.000	0.000
2-122-122- 2	0.006	0.000	0.000	0.006	0.000	0.000
2-122-122-123	0.006	0.000	0.000	0.006	0.000	0.000
2- 2-122-123	0.006	0.000	0.000	0.006	0.000	0.000
1- 2-122-122	0.006	0.000	0.000	0.006	0.000	0.000
122-122-122-123	0.006	0.000	0.000	0.006	0.000	0.000
1- 1- 2-122	0.002	0.000	0.000	0.006	0.000	0.000

TABLE IE.
Torsion-Stretch (Type 1) (TS) Parameters

	K_{ts1}	K_{ts2}	K_{ts3}
X—1—2—Y	0.000	0.000	2.159

TABLE IF.
Improper Torsion (Impt), Torsion-Impt (Timpt), and Impt-Torsion-Impt (Ittit) Parameters.

	Improper Torsion (impt)	Torsion- impt	Impt-torsion- impt
2	1	1.20	5.0
122	123	1.20	5.0
2	112	1.20	5.0
122	112	1.20	5.0
122	122	1.20	5.0
2	2	1.60	5.0

TABLE IG.
Torsion-Torsion (TT) Parameters.

	K_{tt}
2	0.85
2	0.85
122	0.85
2	0.85
2	0.85
2	0.85
122	0.85

TABLE IH.
Stretch-Bend (SB) Parameters.

	K_{sb}
$\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^2}-\text{C}_{\text{sp}^3}$	0.14
$\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^2}-\text{H}$	0.20

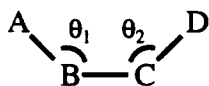


FIGURE 1. Illustration of bend-torsion-bend.

Improper Torsion (Impt)

The improper torsion potential function replaces the out-of-plane bending potential in MM3 and describes the planarity of the sp^2 atom. This term has previously been used in other force fields, such as AMBER.¹³ The new functions in MM4 simplify the calculation for out-of-plane bending, especially for the full matrix optimization, while managing the planarity as well as in MM3. For each sp^2 atom B, there are three improper torsion angles $B-C-A-E$, $B-A-E-C$, and $B-E-C-A$ (see Fig. 2). Therefore, the improper torsion energy around the center atom B will be the sum of the following three energies [eq. (6d)], as shown in eqs. (6a)–(6c), where $K(\omega)$'s are improper torsion force parameters in kcal/mol and ω 's are the respective improper torsion angles in degrees.

$$E(B-C-A-E) = K(B-E) * (1.0 - \cos 2\omega_1) \quad (6a)$$

$$E(B-A-E-C) = K(B-C) * (1.0 - \cos 2\omega_2) \quad (6b)$$

$$E(B-E-C-A) = K(B-A) * (1.0 - \cos 2\omega_3) \quad (6c)$$

$$E_{\text{impt}} = E(B-C-A-E) + E(B-A-E-C) + E(B-E-C-A) \quad (6d)$$

In MM4, a unique force parameter is assigned for each improper torsion type (as defined by the first and last atom type of the improper torsion). For example, MM4 assigns the same force parameter (type 2-112) for improper torsions 2-2-2-112 and 2-1-2-112.

Torsion-improper torsion (timpt)

This term [eq. (7)] "flattens" the C_{sp^2} groups of ethylene and similar molecules. In MM3, as the

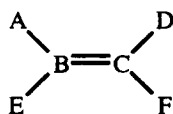


FIGURE 2. Illustration for Impt, Timpt, and Titit.

$H-C_{sp^2}=C_{sp^2}-H$ torsion angle is rotated toward 90° , the C_{sp^2} begins to pucker out of the plane or pyramidalize (see Fig. 3). Some *ab initio* studies suggested that the transition state of ethylene should have D_{2d} symmetry, with bond C_{sp^2} carbons planar.^{14,15}

The MM3 transition state for ethylene is strongly pyramidalized. Although this term does not prevent the pyramidalization of the C_{sp^2} upon rotation in MM4, it does force the C_{sp^2} to become more planar than it otherwise would be, and it increases the energy of the barrier to rotation. A large force constant would dramatically increase the energies of nonplanar compounds in an unrealistic way. Thus, for MM4 a small value for the timpt term is implemented, with the resulting transition state for ethylene-type molecules still containing a pyramidalized C_{sp^2} with the $H-C_{sp^2}=C_{sp^2}-H$ torsions near 60° . However, the C_{sp^2} carbons are somewhat flattened, and the ethylene-type barriers are much improved through the use of this term. The MM4 ethylene energy barrier and timpt term are discussed further in the rotational barrier discussion section.

$$E_{\text{timpt}} = (1 - \cos^2 \omega) * [K_{\text{timpt1}} * (1 - \cos \omega_1) + K_{\text{timpt2}} * (1 - \cos \omega_2)] \quad (7)$$

The value ω is the dihedral angle $A-B-C-D$, ω_1 is the improper torsion angle $B-A-E-C$, ω_2 is the improper torsion angle $C-F-D-B$, K_{timpt1} is the timpt parameter for ω_1 , and K_{timpt2} is the timpt parameter for ω_2 .

Improper torsion-torsion-improper torsion (ittit)

This term [see eq. (8)] mainly adjusts out-of-plane bending frequencies and is similar to the bend-torsion-bend interaction in saturated systems and alkenes. For instance, ethylene's B_{2g} vibrational frequency is calculated too high without this correction. The value K_{ittit} is the ittiti parameter, and the other definitions are the same as those for



FIGURE 3. Locally pyramidalized and locally planar twisted ethylene.

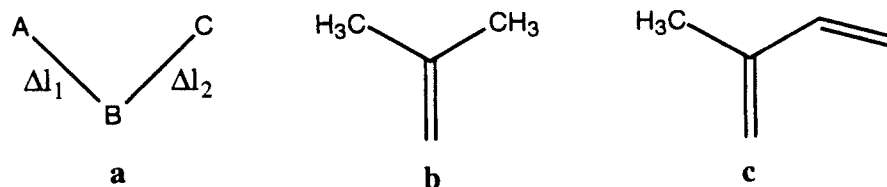


FIGURE 4. Illustration of stretch-stretch.

timpt. This term is discussed further in the following article on conjugated hydrocarbons.^{7a}

$$E_{\text{ittit}} = K_{\text{ittit}} * \cos(\omega_1) * \cos(\omega) * \cos(\omega_2) \quad (8)$$

Stretch-stretch (ss)

The stretch-stretch cross-term is shown in eq. (9) (see Fig. 4a). The stretch-stretch parameter (K_{ss}) is defined such that when a type 1 atom (C_{sp^3}), or any atom type other than 2 (C_{sp^2}), is attached to a type 2 central atom, K_{ss} has a value of 0.4 mdyne/Å (e.g., Fig. 4b). The value of K_{ss} is doubled when a type 2 atom is attached to a type 2 central atom ($K_{ss} = 0.8$, e.g., Fig. 4c). The constant is taken to be zero when a type 1 central atom is involved.

$$E_{ss} = 143.88 * K_{ss} * \Delta l_1 * \Delta l_2 \\ (\Delta l_1 = l_1 - l_1^0, \Delta l_2 = l_2 - l_2^0) \quad (9)$$

This term affects stretches that are coupled to each other with a common atom at the center (symmetric and asymmetric stretches). Isobutene and benzene are especially affected by this term.^{7b}

Torsion-bend (tb)

The purpose of this term [eq. (10)] is to open bond angles, such as C—C—O, C—C—N, C—C—S, and C—C—P, further when a conformation goes from anti to gauche, which would occur with a negative K_{tb} value (torsion-bend parameter); a positive K_{tb} would reduce this angle. Note that K_{tb} is defined by θ . For instance, in butadiene, a positive K_{tb1} term reduces angles $C_1-C_2-C_3$ and $C_2-C_3-C_4$ (type 2-2-2) for the $C_1-C_2-C_3-C_4$ (ω) cis or gauche conformation but does not affect these angles in the trans conformation (see Fig. 5). This term is also very important when atoms containing a lone pair of electrons are involved (related to the Bohlmann effect).

$$E_{tb} = 2.51124 * \{ [K_{tb1}(1 + \cos \omega) \\ + K_{tb2}(1 - \cos 2\omega) + K_{tb3}(1 + \cos 3\omega)] \Delta \theta_1 \\ + K_{tb1}[(1 + \cos \omega) + K'_{tb2}(1 - \cos 2\omega) \\ + K'_{tb3}(1 + \cos 3\omega)] \Delta \theta_2 \} \quad (10)$$

Also, the boat/tub forms of cycloheptatriene and cyclooctatetraene are favored and become more puckered with a positive K_{tb1} term.

Torsion-stretch (ts)

There are two types of torsion-stretch interactions in the MM4 program. One is the variation of the bond length of a central bond identified by the torsional angle, which is called type 1 ts. The second one is identified by the bond length of a terminal bond of the torsional angle, which is called type 2 ts. Type 2 is important for the compounds having a lone pair electrons (the Bohlmann effect) and also for compounds with double bonds (hyperconjugation). This latter term will be discussed further in a subsequent manuscript. Type 1 ts in MM4 is described by eq. (11).

$$E_{ts1} = -k * \Delta l [K_{ts1} * ((1 + \cos(\omega)) \\ + K_{ts2} * ((1 - \cos(2\omega)) + K_{ts3}((1 + \cos(3\omega))))] \quad (11)$$

A threefold parameter, K_{ts3} , was found to be necessary for alkenes, which results in bond stretchings for eclipsed and skew conformations, and the bond length is then relatively shorter for gauche and anti conformations.

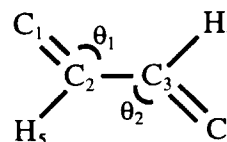


FIGURE 5. Illustration of torsion-bend for butadiene.

Torsion-torsion (tt)

Equation (12) (see Fig. 6) couples torsion angles that share a common bond angle. For instance, the torsions ω_1 and ω_2 are coupled (they share the common bond angle $i-j-k$). The constants (K_{tt}) correspond to their respective torsion angle types. P_{ij} (P_{jk}) is the bond order.

$$E_{tt} = -K_{tt1}(1 - P_{ij})(1 + \cos 3\omega_1)K_{tt2}(1 - P_{jk}) \times (1 + \cos 3\omega_2) \quad (12)$$

This cross-term is important for increasing out-of-plane $C_{sp^2}-C_{sp^2}-C_{sp^2}$ bending frequencies, especially for benzene. It also lowers the (relative) energies of compounds that are more highly aromatic (i.e., have nearly equal adjacent bond orders). This is important for calculating heats of formation in better agreement with experiment. Although theoretically the VESCF calculation should include the effects of resonance energies in the calculated electronic energies of all conjugated compounds, ring systems with all bonds containing equal or nearly equal bond orders seem to be more stable relative to compounds which are only slightly (or negatively) aromatic (e.g., cyclooctatetraene). Intuitively, a twofold term would be expected here, but it was found that a threefold term fit the data better, and hence was used. The tt term is discussed further in the following article.⁷

Van der Waals Interactions

These are crucial in any force field, and they are not obtainable from any direct experiment. Over the years, force fields have gotten better, and van der Waals potentials have changed, substantially since the early 1970s, and more modestly in recent years.^{1,11,16,17}

MM4 includes the same van der Waals function that was used for MM3, but with slightly different parameters. The alkane and olefinic carbons are given separate van der Waals parameters, as in MM3. The alkene carbon parameters were initially chosen by fitting the structure and compressibility of graphite¹⁸ and were then modified slightly to fit crystal packing data better for aromatic hydrocarbons (see Table II). Determining individual van der Waals parameters in this manner seems to be

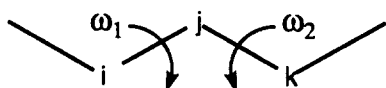


FIGURE 6. Illustration for torsion-torsion.

adequate for modeling nonbonded interactions but is also somewhat approximate, since these carbon and hydrogen parameters cannot be separately measured by experiment, and three-body and higher interactions are ignored.

Unlike for MM3, the parameters for hydrogens attached to alkane and olefinic carbons are now different for MM4. Since the individual C_{sp^3} - and C_{sp^2} -type carbon atom types are separated, it logically follows that hydrogen atom types for each respective carbon should also be treated individually. Although in most cases the same parameters could have been used for hydrogens attached to either carbon type, various problems arise with crystal structures and spectra of conjugated molecules when this is done. Accordingly, the alkane hydrogen (type 5) and the alkene type hydrogen (now type 112 in MM4) were treated separately.

The van der Waals parameters for C_{sp^3} , C_{sp^2} , $H_{C_{sp^2}}$, and $H_{C_{sp^3}}$ are listed in Table III for MM3 and MM4. In general, the van der Waals radius between two different atoms is the sum of the van der Waals radii of each atom; the value for ϵ is the square root of the product of the corresponding ϵ 's. However, in order for MM3 and MM4 to reproduce experimental data better, actual heteronuclear van der Waals parameters need to be adjusted further. In MM3, the type $C_{sp^3} \cdots H$ radius was reduced by about 4% from its averaged value. For MM4, the type $C_{sp^2} \cdots H$ interaction ($2 \cdots 5$) is most significantly affected: The epsilon (ϵ) is increased 55% and the radius is reduced 11%. The $2 \cdots 112$ ϵ and r values are essentially unchanged (from the MM3 values).

Dipole Moments of Alkenes

The dipole parameters are virtually the same for MM4 as MM3. The bond dipole for $C_{sp^3}-C_{sp^2}$ is assigned as 0.95 D (0.90 D MM3), and $H-C_{sp^2}$ has a value of 0.60 D (as in MM3). The dipole parameters are important not only for calculating dipole moments and energies, but also for deter-

TABLE II. Graphite Measurements.

	Experiment	MM4
Space	3.354 Å	3.373 Å
Compressibility	2.97×10^{-12} cm ² /dyn	2.78×10^{-12} cm ² /dyn
Energy	-2.2 kcal/mol	-2.66 kcal/mol

TABLE III.
Van der Waals Parameters.

Atom	Atom Type	MM3 ϵ	MM3 Radius	MM4 ϵ	MM4 Radius
C _{sp} ³	1	0.027	2.03	0.037	1.96
C _{sp} ²	2	0.056	1.96	0.057	1.96
H	5	0.020	1.62	0.017	1.64
H	112	—	—	0.017	1.64
C _{sp} ³ ... H	1 ... 5	0.023	3.51	0.024	3.44
C _{sp} ² ... H	2 ... 5	0.0335	3.58	0.048	3.20
C _{sp} ² ... H	2 ... 112	—	—	0.034	3.58

mining crystal packing forces. All of the experimental dipole moments in Table IV were determined from dielectric constant measurements.

Geometries

As in MM3, all bond lengths are fit to electron diffraction (r_g) bond lengths. Since MM4 determines and prints out the various other kinds of r values needed for comparison with electron diffraction, *ab initio*, and X-ray data, one can readily make the comparisons with experiment or *ab initio* data by using the proper values. Bond lengths given in this article will always be r_g unless otherwise specified.

The general accuracy of MM4 is similar to that of MM3 for structures. Bond lengths are, for the most part, expected to be within about 0.004 Å of the experimental values, and bond angles are accurate to within about 1°, for heavy atoms. The quantities for hydrogens are much less accurate. Moments of inertia are much improved for MM4 compared to MM3. In this case the experimental value to be compared is r_z . We noted earlier that r_g values give moments of inertia which are 0.5–1% larger than the experimental (microwave) values.^{1a} However, r_z values should be close to experiment, and with MM4 they are found to be about ±0.5%. Some discrepancy is expected, because the microwave values are from the rotational ground state, whereas the MM4 values are averaged over the occupied rotational states. The torsion-bend interaction and an electronegativity term are added to MM4 in order to improve geometries. The positive torsion-bend parameters used for alkenes and conjugated hydrocarbons reduce the bond angles contained in a *cis* dihedral angle, leaving the *trans* conformer unaffected. Improvements in alkene moments of inertia result from inclusion of these terms. The electronegativity

effect term increases I_0 of any C_{sp}²—C_{sp}² bond by 0.002 Å for a C_{sp}³ attached to the C_{sp}² carbon; no change is introduced for an attached hydrogen.

STRUCTURES

As previously mentioned, bond length and bond angle deviations from experiment seem similar for MM3 and MM4 and comparable to the errors of the experiment. Structural data, including bond lengths, bond angles, and torsional angles for alkenes, are presented in Tables V–XXVI (also see Fig. 7). Most of the compounds in Tables V–XXVI (Tables XII–XV, XVIII, XXII–XXIV, and XXXII–XXXVII, appear only in Supplementary Material) were discussed in detail in the MM3 papers,^{2,3} and this discussion will not be repeated. The most important improvements in structure come in the moments of inertia, especially for propene, *skew*- and *cis*-1-butene, and *cis*-2-butene.

Tetra-*t*-Butylethylene

This compound (see Fig. 7) has not been synthesized and thus has no experimentally determined geometry. Applying the MM3 and MM4 programs to this molecule shows that the most favorable

TABLE IV.
Dipole Moments of Alkenes (Debye).

	Expt. ^a	MM3	MM4
<i>skew</i> -1-butene	0.30	0.284	0.335
<i>cis</i> -1-butene	0.37	0.271	0.321
<i>cis</i> -2-butene	0.33	0.366	0.455
isobutene	0.503 ± 0.009	0.341	0.401
1,4-pentadiene	0.38 ± 0.02	0.270	0.348
cyclopentene	0.98	0.416	0.800

^a See ref. 19. All experimental results are gas phase except for 1,4-pentadiene (benzene) and cyclopentene (hexane).

TABLE V.
Ethylene.^a

	Expt.	MM4	Δ	MM3	Δ
C=C	1.337	1.337	+0.000	1.337	0.000
C—H	1.103	1.104	+0.001	1.102	-0.001
C=C—H	121.4	120.9	-0.5	120.9	-0.5

^a See ref. 20, ED, r_g bond lengths.**TABLE VI.**
Propene.^a

		Expt.	MM4	Δ	MM3	Δ
C=C	a	1.342	1.340	-0.002	1.339	-0.003
C—C	b	1.506	1.506	0.000	1.504	-0.002
C—H vinyl	c	1.104	1.104	0.000	1.102	-0.002
C—H me	d	1.117	1.112	-0.005	1.113	-0.004
C=C—C	ab	124.3	124.7	+0.4	124.3	0.0
(C=C—H) _{av}	ac / ac'	121.3	120.9	-0.4	120.9	-0.4
C=C—C—H	abd	—	0.0	—	0.2	—
C—C _{av} ^b		1.424	1.423	-0.001	1.421	-0.003

^a See ref. 21, ED, r_g bond lengths.^b Average bond length (C=C, C—C).**TABLE VII.**
skew-1-Butene.^a

		Expt.	MM4	Δ	MM3	Δ
C=C	a	1.340	1.340	0.000	1.339	-0.001
C—C	b	1.502	1.507	+0.005	1.506	+0.004
	c	1.535	1.540	0.005	1.534	-0.001
C—H	d	—	1.104	—	1.104	—
	e	1.114	1.113	-0.001	1.113	-0.001
C=C—C	ab	125.6	124.6	-1.0	124.4	-1.2
C—C—C	bc	111.7	111.8	+0.1	111.9	-0.2
(C=C—H) _{av}	ad / ad'	122.6	120.9	-1.7	120.9	-1.7
C—C—H	ce	111.5	111.3	-0.2	111.4	-0.1
C=C—C—C	abc	119.9	120.2	+0.3	114.5	-5.4
C—C _{av} ^b		1.459	1.462	+0.003	1.460	+0.002

^a See ref. 22, ED, r_g bond lengths (gauche predominates).^b Averaged over cis / gauche using MM4 structures.**TABLE VIII.**
cis-1-Butene.^a

	Num.	Expt.	MM4	Δ	MM3	Δ
C=C	a	1.340	1.341	+0.001	1.340	0.000
C—C	b	1.502	1.510	+0.008	1.507	+0.005
	c	1.526	1.534	+0.008	1.534	+0.008
C—H	d	1.104	1.105	+0.001	1.103	-0.001
	e	1.104	1.113	+0.009	1.113	+0.009
C=C—C	ab	127.2	126.2	-1.0	126.6	-0.6
C—C—C	bc	114.9	115.5	+0.6	116.0	+1.1
C—C _{av} ^b		1.456	1.462	+0.006	1.460	+0.004

^a See ref. 22, ED, r_g bond lengths.

TABLE IX.
cis-2-Butene.^a

	Num.	Expt. (r_a)	Expt. (r_g)	MM4	Δ (r_g)	MM3	Δ (r_g)
C=C	b	1.346	1.348	1.344	-0.004	1.342	-0.006
C—C	a	1.506	1.508	1.507	-0.001	1.505	-0.003
C—C=C	ab	125.4	—	127.2	+1.8	127.4	+2.0
C—C—H	ac	—	—	113.4	—	113.3	—
	ad	110.5	—	110.4	-0.1	110.7	+0.2
C=C—C—H	bac	4.9	—	0.0	-4.9	1.4	-3.5
C—C _{av}		1.453	1.455	1.452	-0.003	1.451	-0.004

^a See ref. 23, ED, r_g bond lengths (corrected from r_a by addition of 0.002 Å, as explained in text).**TABLE X.**
trans-2-Butene.^a

	Num.	Expt. (r_a)	Expt. (r_g)	MM4	Δ (r_g)	MM3	Δ (r_g)
C=C	b	1.347	1.349	1.342	-0.007	1.341	-0.008
C—C	a	1.508	1.510	1.506	-0.004	1.504	-0.006
C—H	c	—	—	1.112	—	1.112	—
	d	—	—	1.106	—	1.106	—
C—C=C	ab	123.8	—	124.6	+0.8	124.3	+0.5
C—C _{av}		1.454	1.456	1.451	-0.005	1.450	-0.006

^a See ref. 23, ED, r_g bond lengths (corrected from r_a , as explained in text).**TABLE XI.**
Isobutene.^a

	Num.	Expt.	MM4	Δ	MM3	Δ
C=C	a	1.342	1.343	+0.001	1.342	0.000
C—C	b	1.508	1.509	+0.001	1.508	0.000
C—H	c	1.095	1.104	+0.009	1.102	+0.007
	d	1.119	1.112	-0.007	1.112	-0.007
C=C—C	ab	122.2	122.5	+0.3	122.2	0.0
C=C—H	ac	121.3	121.0	-0.3	121.1	-0.2
C—C _{av}		1.453	1.454	+0.001	1.452	-0.001

^a See ref. 24, ED, r_g bond lengths.

equilibrium structure results in the *t*-butyl groups on the ethylene carbons having to twist and con-tort in order to avoid close H···H contacts. However, MM3 and MM4 give significantly different geometries. Geometry comparisons are given in Table XXVI. Although both determine the energy minimum to correspond to a C_2 structure, the *t*-butyl groups are twisted nearly 90° from each other in the MM3 structure, with the C_{sp^2} carbons nearly planar. However, in MM4 the *t*-butyl groups are twisted approximately 60°, with the C_{sp^2} carbons slightly puckered (improper torsion angles of 4°). This difference is mainly due to the increased

value of the V2 term for the double bond, coupled with the negative V4 term in MM4, which disfavors rotation of the substituents out of plane, but favors puckering of C_{sp^2} carbons upon rotation about C_{sp^2} — C_{sp^2} bonds. The MM4 structure is believed to be closer to reality.

MOMENTS OF INERTIA

Moments of inertia calculated directly by MM4 correspond to r_g bond lengths. Since experimental moments of inertia are usually determined from microwave studies which determine r_z bond dis-

TABLE XVI.
Cyclohexene.^a

	Num.	Expt. (r_a)	Expt. (r_g)	MM4	Δ (r_g)	MM3	Δ (r_g)
C=C	a	1.341	1.343	1.344	+0.001	1.342	-0.001
C—C	b	1.503	1.505	1.511	+0.006	1.508	+0.003
	c	1.535	1.537	1.538	+0.001	1.537	0.000
	d	1.535	1.537	1.533	-0.004	1.533	-0.004
C—C=C	ab	124.0	—	123.3	-0.7	123.3	-0.7
C—C _{av}		1.492	1.494	1.496	+0.002	1.494	0.000

^a See ref. 29, ED, r_g bond lengths (corrected from r_a , as explained in text).

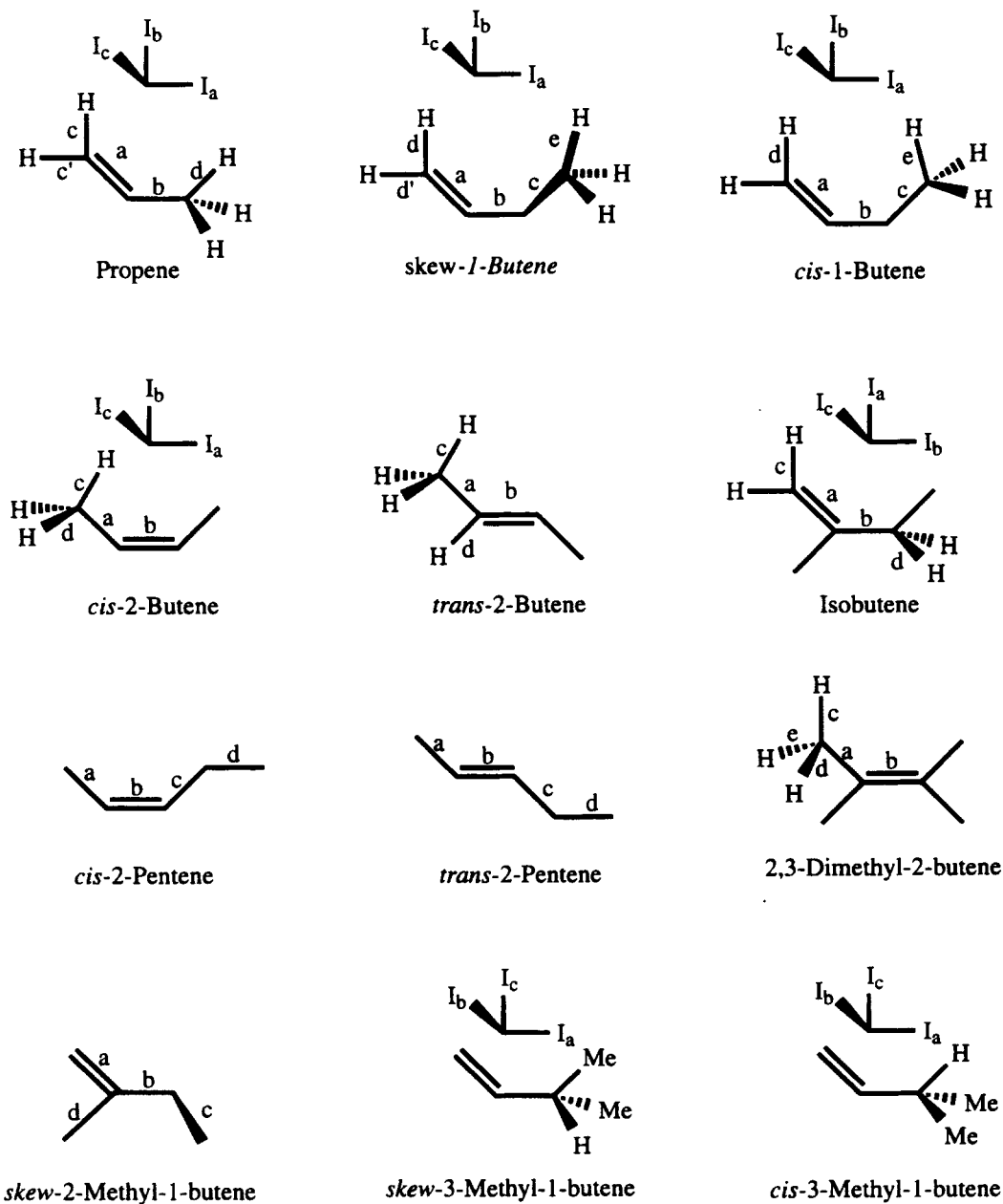


FIGURE 7. Structures and labeling for alkenes.

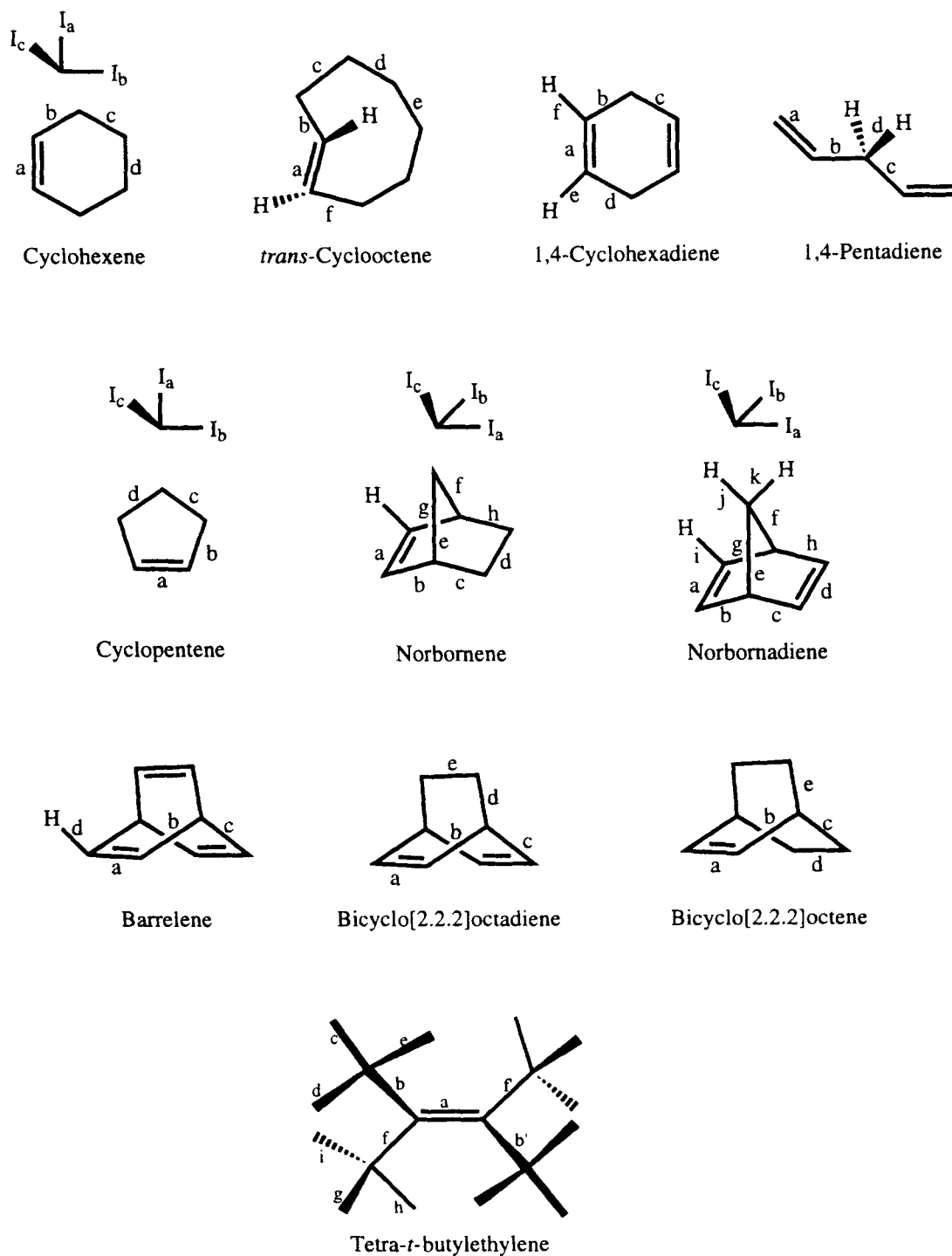


FIGURE 7. (continued)

TABLE XVII.
trans-Cyclooctene.

	Num.	Expt. ^a	Expt. ^b	MM4	MM3
C=C	a	1.332	1.341	1.341	1.340
C—C	b	1.499	1.483	1.499	1.501
	c	1.549	1.543	1.557	1.545
	d	1.549	1.545	1.558	1.553
	e	1.549	—	1.571	1.566
C—C=C	ab	121.9	121.1	119.5	118.8
C—C—C	bc	104.6	105.3	105.0	107.2
	cd	113.8	115.7	115.1	115.2
	de	118.8	118.5	117.2	116.8
C—C=C—C	baf	138.1	139.8	142.5	135.9
H—C=C—H	HaH	177.2	174.6	173.9	173.2
C—C _{av}		1.509	1.498	1.517	1.509

^a See ref. 30, ED, r_a bond lengths.^b See ref. 31, ND (neutron diffraction), r_a bond lengths.**TABLE XIX.**
1,4-Pentadiene.^a

	Num.	Expt.	MM4	Δ	MM3	Δ
C=C	a	1.336	1.340	+0.004	1.339	+0.003
C—C	b	1.501	1.506	+0.005	1.505	+0.004
C—H	d	1.074	1.113	+0.039	1.114	+0.040
C—C=C	ab	125.0	124.6	−0.4	124.4	−0.6
C—C—C	bc	113.0	111.9	−1.1	112.8	−0.2
C—C _{av}		1.419	1.423	+0.004	1.422	+0.003

^a See ref. 34, ED, r_a bond lengths.

tances, the MM4 r_g moments of inertia are generally from 0.5 to 1.0% larger than experiment. Thus, r_g distances are also converted to r_z ones by MM4, so that r_z moments of inertia can be determined for direct comparison to microwave experiments, which should deviate by $\pm 0.5\%$ or so from experiment. Correction factors result from the anharmonicity of the intramolecular potential and displacement due to vibrational excitation. The method utilized by MM4 for bond distance (r_g , r_a , r_z , etc.) corrections has been detailed by Nakata et al.⁴¹ MM4 r_g and r_z moments of inertia for alkenes and conjugated hydrocarbons are reported along with the experimental and MM3 results in Tables XXVII–XXXVII (some in Supplementary Material).

Overall, the MM4 results are either similar to or improved from those of MM3. Some of the MM4 r_z moments of inertia for *skew*-1-butene and *cis*-3-methyl-1-butene are calculated as much as 0.7% lower than experiment, a larger deviation than one

would expect. This is partially due to the problem of determining the degree of rotation for the alkyl group(s) about the $C_{sp^2}-C_{sp^3}$ bond. These moments of inertia are sensitive to the $C_{sp^2}-C_{sp^2}-C_{sp^3}-C_{sp^3}$ torsional terms, whose final values were determined as a compromise of experimental deviations from rotational barrier data and heats of formation, as well as the moments of inertia. The MM4 moments of inertia for norbornadiene also show larger deviations than usual from experiment. A larger stretch-bend term for five-membered rings would improve these results, but at the expense of saturated five-membered ring structures. The energies and geometries of five-membered ring alkenes (especially for strained compounds) are affected by relevant bending force constants and natural bond angles. A compromise for these parameters allows for the best fit of geometries and moments of inertia as well as the heats of formation for unsaturated

TABLE XX.
Cyclopentene.^a

	Num.	Expt. (r_a)	Expt. (r_g)	MM4	Δ (r_g)	MM3	Δ (r_g)
C=C	a	1.343	1.345	1.344	-0.001	1.340	-0.005
C-C	b	1.519	1.521	1.518	-0.003	1.519	-0.002
	c	1.546	1.548	1.552	+0.004	1.551	+0.003
C-C=C	ab	111.0	—	111.3	+0.3	111.9	+0.9
C-C-C	bc	103.0	—	103.6	+0.6	102.2	-0.8
	cd	104.0	—	104.0	+0.0	105.7	+1.7
C-C _{av}		1.495	1.497	1.497	0.000	1.496	-0.001

^a See ref. 35, ED, r_a bond lengths.**TABLE XXI.**
Norbornene.^a

	Num.	Expt.	MM4	Δ	MM3	Δ
C=C	a	1.336	1.348	+0.012	1.343	+0.007
C-C	b	1.529	1.532	+0.003	1.534	+0.005
	c	1.550	1.559	+0.009	1.550	0.000
	d	1.556	1.573	+0.017	1.569	+0.013
	e	1.566	1.545	-0.021	1.544	-0.022
C-C-C	ef	95.3	94.1	-1.2	95.1	-0.2
C-C=C	ab	—	107.3	—	107.7	—
C-C _{av}		1.523	1.524	0.001	1.521	-0.002
	bag & cdh ^b	110.8	111.7	+0.9	111.7	+0.9
	bag & ef ^b	122.3	126.6	+4.3	125.2	+2.9

^a See ref. 36, ED, r_g bond lengths and MW (microwave).^b Angle between planes which includes the following torsions and / or angles.

five-membered rings. The moments of inertia for alkenes are given in Tables XXVII-XXXVII; their orientations are shown in Figure 7.

Conformational Analysis^{||}

Rotational barriers and energy differences have been calculated with MM4 for selected alkenes and compared to experiment. MM3 determines energy barriers and energy differences between conformations from the computed final steric energies for alkenes and from final energies^{||} for conjugated hydrocarbons. The final steric energies, however, neglect explicit inclusion of the vibrational contributions. It was assumed that the vibrational en-

^{||} All *ab initio* calculations were carried out with Gaussian92, and structures were optimized at the 6-31G*/MP2 level, unless otherwise stated (see ref. 78).

[¶] The final energy equals the sum of the final steric energy plus the electronic energy and sigma stretch contribution (from the VESCF calculation) in conjugated molecules.

ergy differences between conformers are small, and these contributions can be absorbed in the bond energy increments for the thermodynamic applications. This approximation was found to be very good in a statistical sense,¹ but it causes problems under certain circumstances. Thus MM4 is now parameterized such that the enthalpies, which include the vibrational energy contributions, should be used to compare different conformations.

At this point it is important to emphasize that how an MM4 energy barrier or difference is calculated depends on the experiment or calculation to which it will be compared. Different experiments measure different quantities. For instance, a nuclear magnetic resonance (NMR) study determines a free energy of activation at a certain temperature, while an *ab initio* calculation (as usually reported) will give the potential energy (not enthalpy) difference for a barrier height or conformational difference. An infrared (IR) study may show a potential

TABLE XXV.
Bicyclo[2.2.2]octene.^a

	Num.	Expt.	MM4	Δ	MM3	Δ
C=C	a	1.341	1.338	-0.003	1.340	-0.001
C—C	b	1.509	1.522	+0.013	1.522	+0.011
	d	1.549	1.558	+0.009	1.556	+0.007
	c	1.549	1.550	+0.001	1.543	-0.006
C—C=C	ab	114.2	114.6	+0.4	114.5	+0.3
C—C—C	bc	107.6	107.1	-0.5	106.9	-0.7
C—C _{av}		1.517	1.522	+0.005	1.519	+0.002

^a See ref. 40, ED, r_g bond lengths.**TABLE XXVI.**
Tetra-*t*-butylethylene.

Bond	MM3	MM4	Angle	MM3	MM4	Torsion	MM3	MM4
a	1.382	1.372	ab	120.1	123.0	bab'	95	122
b	1.556	1.564	af	120.0	119.0	b'af	-88	-65
f	1.552	1.557	bf	119.8	117.7	abc	96	79
c	1.556	1.551	bc	113.9	120.2	abd	-142	-155
d	1.550	1.559	bd	114.1	113.8	abe	-24	-45
e	1.553	1.558	be	112.9	106.5	baf'	-82	-50
g	1.561	1.557	fg	115.3	118.3			
h	1.552	1.551	fh	112.3	114.0			
i	1.554	1.566	fi	113.0	107.5	abf ^a	0.9	3.8

^a Out-of-plane bending of C_{sp²} (improper torsion angle abf and ab'f).**TABLE XXVII.**
Propene.^a

	la	%	lb	%	lc	%
exp.	10.970		54.327		62.149	
mm3	11.168	+1.8	54.589	+0.48	62.503	+0.60
mm4 (r_g)	11.137	+1.52	54.804	+0.88	62.678	+0.85
mm4 (r_z)	10.978	+0.07	54.612	+0.52	62.378	+0.37

^a See ref. 42; units are amu * Å².**TABLE XXVIII.**
skew-1-Butene.^a

	la	%	lb	%	lc	%
exp.	22.411		121.630		124.631	
mm3	23.648	+5.5	121.122	-0.42	123.221	-1.1
mm4 (r_g)	22.862	+2.01	122.552	+0.76	125.529	+0.72
mm4 (r_z)	22.386	-0.11	121.154	-0.39	124.149	-0.39

^a See ref. 22a; units are amu * Å².

TABLE XXIX.
cis-1-Butene.^a

	la	%	lb	%	lc	%
exp.	33.036		90.679		117.479	
mm3	33.165	+0.39	92.302	+1.79	118.992	+1.29
mm4 (r_g)	33.401	+1.10	91.597	+1.01	118.513	+0.88
mm4 (r_z)	33.016	-0.06	91.100	+0.46	117.787	+0.26

^a See ref. 22a; units are amu * Å².**TABLE XXX.**
cis-2-Butene.^a

	la	%	lb	%	lc	%
exp.	31.412		98.222		123.605	
mm3	31.611	+0.63	99.734	+1.5	124.855	+1.3
mm4 (r_g)	31.815	+1.28	99.432	+1.23	124.742	+0.92
mm4 (r_z)	31.312	-0.32	98.141	-0.08	123.347	-0.21

^a See ref. 43; units are amu * Å².

energy curve which reproduces the relevant frequencies for different conformations or, if it is a variable-temperature analysis, it may determine the enthalpy difference directly. Thus, MM4 calculates energies, enthalpies, and free energies, and the appropriate quantity needs to be chosen for comparison with experimental or *ab initio* values.

When comparing conformers which are minima on the energy surface, the enthalpy (the Boltzmann distribution over occupied vibrational levels) difference is taken directly. However, when examining a rotational barrier to compare with experiments which measure energies from the bottom of the well (e.g., most IR experiments which are not temperature dependent), the energy between the zero and first vibrational level must be subtracted from the compound which is the minimum. This energy is $1/2h\nu$, where ν is the frequency of the minimum energy conformer corresponding to the negative eigenvalue of the transition state F matrix. The results obtained by MM4 are similar to or better than those from MM3. When an experiment reports ΔH or ΔG values, the corresponding MM4 quantity is presented for direct comparison.

Alkenes

The alkene results are reported in Table XXXVIII. Many of them have been discussed previously, and that discussion will not be repeated.^{2,48}

The Ethylene Barrier

Activation energies (ΔE_a 's) of rotation about the double bond in ethylene,⁵⁶ *cis*-2-butene,⁵⁶ *cis*-2,2,5,5-tetramethyl-3-hexene,⁵⁷ and *cis*-2,2,3,4,5,5-hexamethyl-3-hexene⁵⁷ have been measured experimentally and are shown in Table XXXIX. The MM4 activation energies are considerably closer to the experimental values than the MM3 values were. The resulting ethylene-type barriers from MM4 are lower than experiment by about 9–19 kcal/mol, while the MM3 results give 30 + kcal/mol deficiencies for these barriers.⁵⁶ This improvement is mainly due to the increased V2 term, coupled with the negative V4 term, with some benefit from the torsion-improper torsion (timpt) term. These terms are discussed further below.

Various states of twisted (perpendicular $\text{CH}_2=\text{CH}_2$) ethylene have been studied with *ab initio* methods.^{14,15,58} These studies describe geometries of twisted ethylene (D_{2d} symmetry, 90° rotation). However, all structures in these *ab initio* studies appear to correspond to excited states of ethylene. Brooks and Schaefer carried out constrained* SCF and two-electron CI (double zeta + d basis) calculations on four excited states: The two lowest states (N state 1B_1 , T state 3A_2) have energies (two-electron CI) of 68.0 and 66.6 kcal/mol

* Pyramidalized ethylene, with the experimental H—C—H angle and C—H bond length, was used as the optimized geometry.

TABLE XXXI.
Isobutene (Me₂C=CHD).^a

	la	%	lb	%	lc	%
exp.	58.151		62.298		114.304	
mm3	58.644	+0.85	62.816	+0.83	114.953	+0.57
mm4 (r _g)	58.750	+1.03	62.781	+0.78	115.006	+0.61
mm4 (r _z)	58.421	+0.46	62.466	+0.27	114.426	+0.16

^a See ref. 44; units are amu*Å²; note that moments of inertia are for the deuterated structure.**TABLE XXXVIII.**
Energy Barriers and Differences for Alkenes (kcal / mol).

Compound	Conformation	Ref.	Exp. ^a	Result	MM3	MM4 ^b
Propene		49	mw	1.994	1.74	1.81
<i>cis</i> -2-Butene		50, 51	hc, mw	0.45, 0.75	0.98	0.98
<i>trans</i> -2-Butene		50, 52	hc, ir	1.95, 1.50	1.72	1.79
Isobutene		52, 53	ir, mw	2.30, 2.21	1.64	2.10
2,3-Dime-2-butene		54	hc	0.68	0.58	0.65
2-Me-2-butene ^c	Gem, trans	52	ir	1.93	1.53	2.02
	Non-gem	—	—	none	0.79	0.80
	Gem, cis	—	—	none	0.73	1.14
Cyclopentene	Envelope / planar	55	ir	0.66	0.68	0.76

^a mw = microwave splitting technique (potential energy difference), hc = heat capacity data (potential energy difference), ir = infrared experiment (not variable temperature) (potential energy difference).^b All MM4 values are computed from potential (final steric) energies in this table.^c For 2-methyl-2-butene, conformer 2 has its *cis* geminal methyl (H) *trans* to the double bond, conformer 3 has its *trans* geminal methyl (H) *trans* to the double bond, conformer 4 has its nongeminal methyl (H) *trans* to the double bond.**TABLE XXXIX.**
Energies of Transition States of Alkenes (kcal / mol).

	Expt. ^a	MM4 ^b	MM3	Temp. (K)
Ethylene	65	50.7	35.6	425–525
<i>cis</i> -2-Butene	62.4	48.5	32.8	385–451
<i>cis</i> -2,2,5,5-Tetramet-3-hexene	54.4 ± 0.7	35.2	23.6	N / A
<i>cis</i> -2,2,3,4,5,5-hexamet-3-hexene	40.4 ± 1.7	31.4	9.3	468–528

^a Arrhenius activation energies (ΔE_a).^b Final steric energy differences.

and the two higher singlets (Z state ¹A₁, V state ¹B₂) have energies of 154.3 and 153.8 kcal/mol above the planar ground state of ethylene.^{14a} The authors state that the N (lowest energy) state corresponds to the rotational barrier of ethylene. The latter two are reported to be highly polarizable zwitterionic methylene dimers, and this is seemingly confirmed by Trinquier and Malrieu, who also report the optimized (both SCF and CI, double-zeta

basis set) geometry of the higher energy singlet.⁵⁸ They discuss the possibility of a barrierless pathway from ground to excited state ethylene. A later study reports a rotational barrier for ethylene, which was obtained by rotating about the double bond.^{14b} The —CH₂ groups remain planar, however, throughout the rotation. (It is not clear if this is because they were held planar due to the method of rotation.) They report a barrier to rotation of

65.0 kcal/mol, with the 90° triplet state having D_{2d} (planar) symmetry.

A simple rotation about an $H-C_{sp^2}=C_{sp^2}-H$ torsion from 0 to 180° in 15° increments at the MP2/6-31G* level of theory with the Gaussian92 program⁷⁸ does not proceed as it does in molecular mechanics. Instead, the hydrogen not being rotated (unrestrained) seems to stay in place (does not rotate along with its geminal hydrogen). The consequence of this is that both C_{sp^2} 's pyramidalize and the energy continues to increase as the torsion proceeds to 180°. Since the unrestrained hydrogen does not rotate with its geminal hydrogen, the molecule becomes increasingly more strained as it is rotated out of the plane. In our hands at least, the program does not deal with this problem in an adequate way. However, it is clear that near the bottom of the potential well, rotation leads to pyramidalization at at least one center.

Whether the lowest singlet excited state of ethylene is involved in the rotational barrier via a torsional or "barrierless" pathway does not seem to be clear. However, if the transition state is indeed an excited state, molecular mechanics would not be expected to be able to address this problem. Currently, the transition state at 90° for MM4 (one of the C_{sp^2} 's pyramidalized and the other planar) is calculated to have an energy 14 kcal/mol below the experimental value (the MM3 value is 29 kcal/mol lower than experiment).

Our conclusion is that we cannot represent as well as we would like the rotational barrier in ethylene, although it is not really clear what the behavior of the geometry near the top of the barrier should be. However, for most purposes (not very near the top of the barrier), we believe that the present MM4 formulation will be adequate.

The Torsion-Improper Torsion Term

The MM3 calculated ethylene-type barriers are lower than experiment in part because the C_{sp^2} puckers upon rotation in order to relieve strain. In what is usually considered to be the actual reaction coordinate, the $C_{sp^2}-C_{sp^2}$ pi-bond breaks and the CH_2 groups are perpendicular to each other in the transition state.¹⁵ Rotation about the double bond causes the C_{sp^2} carbon to pyramidalize (pucker) with MM3, and the torsion angles in the transition state (C_s symmetry, Fig. 8) occur near 60° instead of the expected 90°. The improper torsion angles are consequently 8°–24° (see Table XL and Fig. 8) in MM3 instead of 0°, and this puckering lowers the MM3 transition state ener-

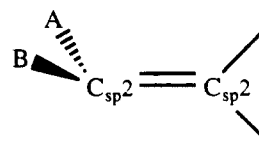


FIGURE 8. Improper torsion angle $C_{sp^2}-A-B-C_{sp^2}$.

gies. The MM4 ethylene-like transition state structures are similar to those from MM3, but the larger V2 terms in MM4 increase the amount of C_{sp^2} puckering in these structures (Table XL).

In MM4, the C_{sp^2} carbon could be forced planar using a very large torsion-improper torsion cross-term (about 35.0 kcal/mol). In this case, the transition state barrier energies would increase to values comparable to experiment and the structures would resemble that of the *ab initio* transition state, with dihedral angles at or near 90°. However, a timpt constant of this magnitude would have undesirable ramifications for the energies of various nonplanar compounds. Also, it is not really certain whether the "true" ethylene transition state is actually planar or pyramidal. An example of C_{sp^2} carbons of a $C=C$ bond pyramidalizing is found in *trans*-cyclooctene.² Thus, the MM4 value for the torsion-improper torsion term was chosen to be 5.0 kcal/mol for C_{sp^3} , C_{sp^2} , and H atom types attached to C_{sp^2} , which helps improve the ethylene-type rotational barriers, but does not affect their transition state structures much or severely distort any of the structures of nonplanar compounds. Planar compounds are unaffected geometrically by the torsion-improper torsion term.

The V4 Term

In MM3, the rotational barriers of the aforementioned substituted ethylenes could have been calculated closer to experiment if the V2 term for the

TABLE XL. Comparison of MM3 and MM4 Improper Torsion Angle $C_{sp^2}-A-B-C_{sp^2}$ in Degrees (see Fig. 8).

	MM4	MM3
Ethylene	36.5	23.9
<i>cis</i> -2-Butene	33.9	20.4
<i>cis</i> -2,2,5,5-Tetramet-3-hexene	33.1	14.3
<i>cis</i> -2,2,3,4,5,5-Hexamet-3-hexene	19.5	8.0

$C_{sp^2}-C_{sp^2}$ central bond had been increased. However, the torsional and out-of-plane bending frequencies would then have increased far too much. Therefore, a V4 term has been added to the torsional potential in MM4 [see eq. (13)].

$$E_{\text{tor}} = 1/2 * V1(1 + \cos \omega) + 1/2 * V2(1 - \cos 2\omega) + 1/2 * V3(1 + \cos 3\omega) + 1/2 * V4(1 - \cos 4\omega) \quad (13)$$

case 1: $V4 = -9\%V2$ for $A-C=C-B$,
where neither A nor B is C_{sp^2}

case 2: $V4 = -6\%V2$ for $A-C=C-B$,
where A and/or B is C_{sp^2}

The V4 potential has maxima at torsion angles of 45° and 135° and minima at torsion angles of 0° , 90° , and 180° . Thus for alkenes, where most ground states are at 0° or 180° and transition states are at approximately 90° , the V2 term can be raised to give better rotational barriers, while a negative V4 term can be added to prevent calculating the torsional frequencies too high. The V4 term will have no effect on the barrier height at 90° , but it will affect the shape of the torsional potential at the ground state, and thus the torsional frequencies.⁹ A negative V4 term results in a broader torsional potential well, and thus lower frequencies. The V4 term also affects torsional and out-of-plane bending frequencies for conjugated systems. Experimental evidence for the presence of a V4 term in ethylene was presented by Wallace.¹⁰ His paper appeared after we had reached the above conclusions. He found that V4 is -12.7% of V2. The value of V4 in MM4 is -9% of V2 for case 1 (alkenes). The MM3 and MM4 V2 values are listed in Table XLI.

Propene

The barrier height to rotation of the methyl group in propene was determined by a thermodynamic method to be 1.95 kcal/mol, and values of 1.978 kcal/mol and 1.994 kcal/mol were determined from microwave splitting techniques.⁴⁹ A calculation at the MP2/6-31G** level with Gaussian92⁷⁸ determined the energy barrier to be 1.98 kcal/mol with a bond lengthening of 0.0088 Å going from the ground to the transition state, demonstrating the $C_{sp^3}-C_{sp^2}$ bond length to be a function of the $H-C_{sp^3}-C_{sp^2}-H$ torsion angle.

TABLE XLI.
Comparison of MM3 and MM4 V2 Torsional Parameters.

Torsion ^a	MM3	MM4
1 2 2 1	9.5	16.0
1 2 2 5	10.0	16.0
5 2 2 5	11.5	16.0
1 2 2 2	7.0	8.5
2 2 2 2	10.0	14.5
2 2 2 5	9.0	14.5

^a Note that in MM4, hydrogens attached to type 2 carbons are assigned atom type 112 (type 5 for MM3).

The corresponding MM4 values are 1.81 kcal/mol and 0.0092 Å.

In general, the torsion-stretch (TS) term, which is present in MM3, operates as a function of the torsion angle of interest, where the term " $1 + \cos 3\omega$ " determines the E_{TS} . An increased energy results in a longer bond length. Normally, the torsion-stretch parameter is assigned to the central bond of the dihedral angle. However, for the dihedral $A-C_{sp^3}-C_{sp^2}-B$ (where the atom types of the central bond are either 1-2 or 1-122), the TS equation is ignored (or the constant is zero) when either A or B is an C_{sp^2} atom type, as in the case of propene. The TS cross-term results in the lengthening of the propene transition state $C_{sp^3}-C_{sp^2}$ bond length, since the $H-C_{sp^3}-C_{sp^2}-H$ torsion angle equals zero. The ground state low-energy conformation of propene is stabilized when one of the methyl hydrogens eclipses the double bond in propene since the $C_{sp^2}-C_{sp^2}-C_{sp^3}-H$ torsion is not involved in the TS equation.

1-Butene and 3-Methyl-1-Butene

Both 1-butene and 3-methyl-1-butene have been studied experimentally and by *ab initio* methods. Note that the conformer designation for 1-butene refers to the $C=C-C-C$ dihedral, while that of 3-methyl-1-butene refers to the $C=C-C-H$ dihedral, as shown in Figs. 9 and 10. The skew and cis forms of 1-butene are both minima. *Ab initio* calculations,^{60,61} microwave,⁶² electron diffraction (ED),⁶³ and low-temperature IR⁶⁴ studies find the skew form to be lower in energy than the cis (hyperconjugation), while a Raman study found the cis to be more stable than skew.⁶⁵ Wiberg and Martin optimized all four structures at the HF/3-21G level,⁶⁰ while Pettersson and Gundertofte used MM2(87).⁶¹ Both then performed single-point calculations using the 6-31G* basis set. The results

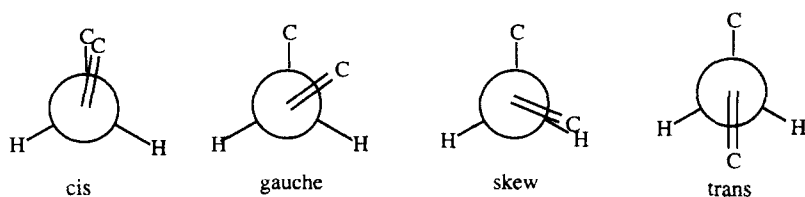


FIGURE 9. 1-Butene.

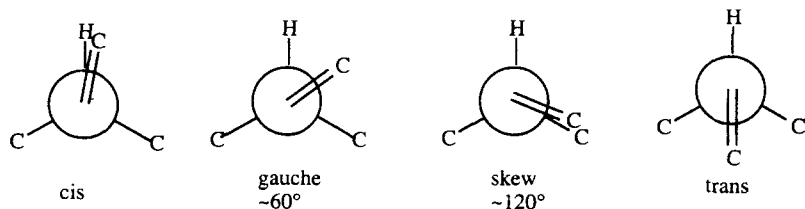


FIGURE 10. 3-Methyl-1-butene.

are summarized in Table XLII (see Supplementary Material). Calculations at the MP2/6-31G**//MP2/6-31G** level for 1-butene from 0° to 180°, with minima located at 117.8° and 0.0° and maxima at 53.6° and 180°, are included in Table XLII. The experimental results (all gas phase) are listed in Table XLIII (see Supplementary Material).

The MM4 results for the barrier to rotation of 1-butene are compared with MP2/6-31G** calculations in Table XLIV, and the MM3 and MM4 energies for 1-butene and 3-methyl-1-butene are listed in Table XLV and correspond to potential energy differences.

The available data for 3-methyl-1-butene include a Raman study⁶⁶ and calculations by Pettersson (same method as 1-butene). The results are reported in Table XLVI. A microwave⁶⁷ and an ¹H-NMR⁶⁸ study, in nonpolar (CS₂, CCl₄) and di-polar (neat liquid) solvent, indicate that the

TABLE XLIV.
Driver Energies of Internal Rotation for
1-Butene (kcal / mol).

C ₁ —C ₂ —C ₃ —C ₄		MP2 / 6-31G**	MM4 ^a
180°	(trans)	2.31	1.72
150°		1.07	0.73
120°	(skew)	0.00	0.00
90°		0.78	0.73
60°	(gauche)	2.11	1.89
30°		1.43	1.35
0°	(cis)	0.45	0.64

^a MM4 values are final steric energy differences.

TABLE XLV.
Minimized Final Steric Energies of 1-Butene
and 3-Methyl-1-Butene (kcal / mol).

Compound	Conformation	MM3	MM4
1-Butene	skew (120.2°)	0	0
	cis	0.69	0.64
	gauche (54.0°)	1.52	1.94
	trans	2.11	1.72
3-Me-1-butene	cis	0	0
	gauche (68.2°)	2.22	2.02
	skew (122.2°)	0.91	0.80
	trans	1.31	1.96

(~ 120° cis) energy difference is 0.37 ± 0.06 and 0.127 ± 0.014 kcal/mol, respectively. The NMR results were determined by fitting coupling constants to consistent force field (CFF)/INDO calculated geometries of the two conformer minima. The NMR results, while of high precision, are of questionable accuracy because of the low-level semiempirical geometry calculations.

TABLE XLVI.
Experimental and *Ab Initio* Conformational
Energies (kcal / mol) for 3-Methyl-1-Butene.

Conformation	Durig ⁶⁶ Raman	Pettersson ⁶¹	
		RHF	MP2
gauche (~ 60°) cis	2.51	2.78	2.54
skew (~ 120°) cis	0.42	1.00	0.85
trans cis	1.31	2.12	1.62

RHF = restricted Hartree-Fock.

Cyclopentene

The barrier height for inversion of cyclopentene has been determined by IR experiments and high-level *ab initio* calculations. Direct observations of ring puckering transitions in the IR spectrum show the barrier to be 232 cm^{-1} (0.66 kcal/mol) with a puckering angle of 23.2° .⁵⁵ An *ab initio* calculation calculated a barrier of 235 cm^{-1} , utilizing an average of basis sets TZ(*d*, *p*) and PZ(3*d*2*f*, 2*p*1*d*) and correlation methods MP2 and MP4.⁶⁹ MP2/DZ(*d*) predicts an angle of 23.6° . MM4 gives a (potential energy) barrier height of 0.76 kcal/mol with an angle of 24.6° .

Cyclohexene

In 1991, energy barriers were reported from a twist angle and bending coordinate two-dimensional potential energy function⁷⁰ (see Fig. 11). A comparison of these results with two previous studies and MM4 appears in Table XLVII, where the twist is the low-energy conformation. The boat conformer is the transition state (at $\tau = 0$), which Rivera-Gaines and coauthors reported as a saddle point on the potential energy surface, and the planar form is a hill top (two negative eigenvalues) on that surface.⁷⁰ The two other IR experiments used only one-dimensional potential functions to determine these energy barriers.

An NMR study reported by Anet and co-workers in 1992 determined the ΔG^\ddagger at -151°C in CBrF_3 solvent to be 5.5 kcal/mol .⁷¹ In the gas

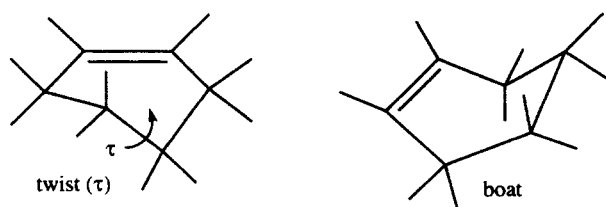


FIGURE 11. Cyclohexene.

TABLE XLVII.
Cyclohexene Conformational Energies (kcal / mol).

	MM4 ^a	NMR ('92) ^b	IR ('91) ^c	IR ('80) ^d	IR ('74) ^e
boat twist	7.3	≤ 7.95	10.3	7.4	7.5
planar twist	13.1	—	13.4	16.6	25.2

^a MM4 results are potential energy differences.

^b See ref. 71 and text.

^c See ref. 70.

^d See ref. 72.

^e See ref. 73.

phase, they could only measure the homoallylic proton signal down to -73°C , and they used the observed line broadening to infer an upper bound to the gas phase interconversion barrier (ΔG^\ddagger) at this temperature to be 7.45 kcal/mol . The upper limit for the potential energy barrier was determined to be 7.95 kcal/mol , which included an entropy estimation from MM3 of 0.6 eu and a zero-point correction from *ab initio* of 0.4 kcal/mol . The MM4 potential energy difference for this barrier is 7.3 kcal/mol , and ΔG^\ddagger is 6.1 kcal/mol at -151°C .

Cycloheptene

The *trans*- to *cis*-cycloheptene interconversion has an experimental activation enthalpy (ΔH_{270}^\ddagger) of $18.2 \pm 1.2\text{ kcal/mol}$.⁷⁴ The MM4 result is 17.7 kcal/mol (MM3 is 16.7 kcal/mol) with a transition state $\text{C}=\text{C}-\text{C}-\text{C}$ torsion angle of 54.8° . The *cis* form is calculated by MM4 to be 28.8 kcal/mol below *trans*-cycloheptene (no experimental data available, but we found that the HF 6-31G** difference is 35.4 kcal/mol . Interestingly, when the calculation was repeated at the MP2 level, the energy difference dropped to 28.3 kcal/mol). The $\text{C}=\text{C}-\text{C}-\text{C}$ torsion angle is 0.0° for the *cis* and 117.9° for the *trans* conformer in MM4.

Four minimum-energy conformers of cycloheptene have been determined by MM4 and are shown in Table XLVIII (Fig. 12). The barrier from the chair to twist conformer (steric energy differences) is 2.69 kcal/mol ; from the chair to boat conformer is 10.90 kcal/mol ; from the twist-boat to boat conformer is 4.57 kcal/mol .

Trans-Cyclooctene

Experimental energy barriers between (+) and (−) *trans*-cyclooctene were determined to be $\Delta E^\ddagger = 35.6 \pm 0.9\text{ kcal/mol}$, $\Delta H^\ddagger = 34.7 \pm 0.9$,

TABLE XLVIII.
Cycloheptene MM4 Conformational Energies
(kcal/mol) Relative to the Chair Form.

Conformation	Energy Difference
Chair	0.00
Twist	0.87
Twist-boat	2.58
Boat	5.26

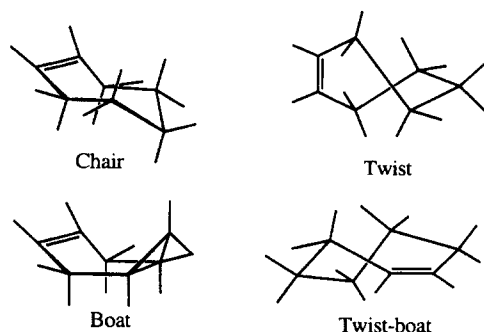
and $\Delta G^\ddagger = 34.9 \pm 0.2$ kcal/mol⁷⁵ at 155.3°C. The transition state for the racemization was found by MM4 to lie 34.7 kcal/mol (ΔG^\ddagger at 155.3°C) above the ground state. The enthalpy difference between *cis*- and *trans*-cyclooctene was determined experimentally to be 11.37 kcal/mol⁷⁶ and by MM3 and MM4 to be 10.78 and 12.21 kcal/mol, respectively. One difficulty with determining the heat of hydrogenation for *trans*-cyclooctene is that it tends to polymerize upon standing, and thus the experimental value may be too low.

1,4-Cyclohexadiene

The analysis of the far infrared spectrum for 1,4-cyclohexadiene led Laane and Lord to conclude that there is a planar ring and thus no barrier to inversion (i.e., a zero barrier).⁷⁷ This result is also obtained from MM4.

Heats of Formation

These quantities are important in defining the force fields for alkenes and for conjugated hydrocarbons.^{1,11} It was more effective to consider both groups of compounds together, and consequently they will both be discussed in the following article.^{7a}

**FIGURE 12.** Four minima for cycloheptene.

Supplementary Material

The package of Supplementary Material referred to in the text (MM4 results for 16 additional compounds) is available from the authors upon request.

Acknowledgments

The authors are indebted to the National Science Foundation (CHE 9222655) and to Tripos Associates for support of this work, to Dr. Jenn-Huei Lii for helpful discussion and assistance with the programming, and to Drs. T. Halgren and J. L. M. Dillen for reading and commenting on the manuscript.

References

- (a) N. L. Allinger, Y. H. Yuh, and J.-H. Lii, *J. Am. Chem. Soc.*, **111**, 8551 (1989); (b) J.-H. Lii and N. L. Allinger, *J. Am. Chem. Soc.*, **111**, 8566 (1989); (c) J.-H. Lii and N. L. Allinger, *J. Am. Chem. Soc.*, **111**, 8576 (1989).
- N. L. Allinger, F. Li, and L. Yan, *J. Comput. Chem.*, **11**, 848 (1990).
- N. L. Allinger, F. Li, L. Yan, and J. C. Tai, *J. Comput. Chem.*, **11**, 868 (1990).
- (a) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963); (b) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **21**, 169 (1965).
- Previous article on alkanes; N. L. Allinger, K. Chen, and J.-H. Lii.
- (a) N. L. Allinger, M. Rahman, and J.-H. Lii, *J. Am. Chem. Soc.*, **112**, 8293 (1990); (b) L. R. Schmitz and N. L. Allinger, *J. Am. Chem. Soc.*, **112**, 8307 (1990), and later articles.
- (a) N. Nevins and N. L. Allinger, "Molecular Mechanics (MM4) Calculations on Conjugated Hydrocarbons," following article; (b) N. Nevins and N. L. Allinger, "Molecular Mechanics (MM4) Vibrational Frequency Calculations for Alkenes and Conjugated Hydrocarbon Systems," second following article.
- (a) L. S. Bartell, *J. Am. Chem. Soc.*, **99**, 3279 (1977); (b) N. L. Allinger, *J. Am. Chem. Soc.*, **99**, 8127 (1977).
- L. Yan, Ph.D. dissertation, University of Georgia, August 1991.
- R. Wallace and J. P. Leroy, *Chem. Phys.*, **144**, 371 (1990).
- U. Burkert and N. L. Allinger, *Molecular Mechanics*, American Chemical Society, Washington, DC, 1982, p. 28.
- C. J. Böttcher, *Theory of Electric Polarization*, Elsevier, Amsterdam, 1952.
- S. J. Weiner, P. A. Kollman, D. A. Case, U. C. Singh, C. Ghio, G. Alagona, S. Profeta, Jr., and P. Weiner, *J. Am. Chem. Soc.*, **106**, 765 (1984).

14. (a) B. R. Brooks and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **101**, 307 (1979); (b) H. Ichikawa, Y. Ebisawa, and A. Shigihara, *Bull. Chem. Soc. Jpn.*, **58**, 3619 (1985).
15. R. Grev, personal communication.
16. U. Dinur and A. T. Hagler, *J. Am. Chem. Soc.*, **111**, 5149 (1989).
17. T. A. Halgren, *J. Am. Chem. Soc.*, **114**, 7827 (1992).
18. N. L. Allinger and J.-H. Lii, *J. Comput. Chem.*, **8**, 1146 (1987).
19. A. L. McClellan, *Tables of Experimental Dipole Moments*, Vol. 2, 1974.
20. L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, Jr., *J. Chem. Phys.*, **42**, 2683 (1965).
21. I. Tokue, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, **17**, 207 (1973).
22. (a) S. Kondo, E. Hirota, and Y. Morino, *J. Mol. Spectr.*, **28**, 471 (1968); (b) D. V. Hemelrijk, L. V. der Enden, H. J. Geise, H. L. Seller, and L. Schäfer, *J. Am. Chem. Soc.*, **102**, 2189 (1980).
23. A. Almenningen, I. M. Anfinsen, and A. Haaland, *Acta. Chem. Scand.*, **24**, 43 (1970).
24. (a) I. Tokue, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, **23**, 33 (1974); (b) L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **39**, 1732 (1963).
25. J. H. M. Ter Brake, *J. Mol. Struct.*, **118**, 63 (1984).
26. J. H. M. Ter Brake and F. C. Mijlhoff, *J. Mol. Struct.*, **77**, 253 (1981).
27. L. Doms, L. van den Enden, and H. J. Geise, *J. Mol. Struct.*, **94**, 241 (1983).
28. T. Shimanouchi, Y. Abe, and K. Kuchitsu, *J. Mol. Struct.*, **2**, 82 (1968).
29. S. Saebo and J. E. Boggs, *J. Mol. Struct.*, **73**, 137 (1981).
30. M. Traetteberg, *Acta. Chem. Scand.*, **B29**, 29 (1975).
31. O. Ermer and S. A. Mason, *Acta. Cryst.*, **B38**, 2200 (1982).
32. G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967).
33. H. Oberhammer and S. H. Bauer, *J. Am. Chem. Soc.*, **73**, 137 (1951).
34. J. H. M. Ter Brake, *J. Mol. Struct.*, **118**, 73 (1984).
35. M. I. Davis and T. W. Muecke, *J. Phys. Chem.*, **74**, 1104 (1970).
36. J. F. Chiang, R. Chiang, K. C. Lu, E.-M. Sung, and M. D. Harmony, *J. Mol. Struct.*, **41**, 67 (1977).
37. A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **44**, 2356 (1971).
38. G. Knuchel, G. Grassi, B. Vogelsanger, and A. Bauder, *J. Am. Chem. Soc.*, **115**, 10845 (1993).
39. S. Yamamoto, M. Nakata, T. Fukuyama, K. Kuchitsu, D. Hasselmann, and O. Ermer, *J. Phys. Chem.*, **86**, 529 (1982).
40. A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **44**, 1783 (1971).
41. M. Nakata, S. Yamamoto, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, **100**, 143, (1983).
42. D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).
43. S. Kondo, Y. Sakurai, E. Hirota, and Y. Morino, *J. Mol. Spectr.*, **34**, 231 (1970).
44. L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **39**, 1732 (1963).
45. R. A. Creswell, M. Pagitsas, P. Shoja-Chaghervand, and R. H. Schwendeman, *J. Phys. Chem.*, **83**, 1427 (1979).
46. L. H. Scharpen, J. E. Wollrab, and D. P. Ames, *J. Chem. Phys.*, **49**, 2368 (1968).
47. G. W. Rathjens, Jr., *J. Chem. Phys.*, **36**, 2401 (1962).
48. F. Li, Ph.D. dissertation, Department of Chemistry, University of Georgia, 1987.
49. E. Hirota, *J. Chem. Phys.*, **45**, 1984 (1966).
50. J. E. Kilpatrick and K. S. Pitzer, *J. Res. Natl. Bur. Std.*, **37**, 163 (1949).
51. (a) T. N. Sarachman, *J. Chem. Phys.*, **49**, 3146 (1968); (b) S. Kondo, Y. Sakurai, E. Hirota, and Y. Morino, *J. Mol. Spec.*, **34**, 231 (1970).
52. J. R. Durig, C. W. Hawley, and J. Bragin, *J. Chem. Phys.*, **57**, 1426 (1972).
53. V. W. Laurie, *J. Chem. Phys.*, **34**, 1516 (1961).
54. D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, J. F. Messerly, R. E. Pennington, and G. Waddington, *J. Am. Chem. Soc.*, **77**, 4993 (1955).
55. J. Laane and R. C. Lord, *J. Chem. Phys.*, **47**, 4941 (1967).
56. J. Saltiel and J. L. Charlton, In *Rearrangements in the Ground and Excited States*, Vol. 3, P. Demayo, Ed., Academic, New York, 1980, p. 25.
57. J. E. Gano, D. Lenoir, B.-S. Park, and R. A. Roesner, *J. Org. Chem.*, **52**, 5636 (1987).
58. G. Trinquier and J.-P. Malrieu, *Chem. Phys. Lett.*, **72**, 328 (1980).
59. (a) N. L. Allinger, R. S. Grev, B. F. Yates, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **112**, 114 (1990); (b) W. Allen, unpublished work.
60. K. B. Wiberg and E. Martin, *J. Am. Chem. Soc.*, **107**, 5035 (1985).
61. I. Pettersson and K. Gundertofte, *J. Comput. Chem.*, **12**, 839 (1991).
62. S. Kondo, E. Hirota, and Y. Morino, *J. Mol. Spectr.*, **28**, 471 (1968).
63. D. V. Hemelrijk, L. van den Enden, H. J. Geise, H. L. Sellers, and L. Schafer, *J. Am. Chem. Soc.*, **102**, 2189 (1980).
64. A. J. Barnes and J. D. R. Howells, *J. Chem. Soc., Faraday Trans.*, **69**, 532 (1973).
65. J. R. Durig and D. A. C. Compton, *J. Phys. Chem.*, **84**, 773 (1980).
66. J. R. Durig and D. J. Gerson, *J. Phys. Chem.*, **85**, 426 (1981).
67. R. A. Creswell, M. Pagitsas, P. Shojachaghervand, and R. Schwendeman, *J. Phys. Chem.*, **83**, 1427 (1979).
68. F. H. A. Rummens, C. Simon, C. Coupry, and N. Lumbroso-Bader, *Org. Magn. Reson.*, **13**, 33 (1980).
69. W. D. Allen, A. G. Csaszar, and D. A. Horner, *J. Am. Chem. Soc.*, **114**, 6834 (1992).
70. V. E. Rivera-Gaines, S. J. Leibowitz, and J. Laane, *J. Am. Chem. Soc.*, **113**, 9735 (1991).
71. F. A. L. Anet, D. I. Freedberg, J. W. Storer, and K. N. Houk, *J. Am. Chem. Soc.*, **114**, 10969 (1992).
72. T. L. Smithson and H. J. Wieser, *J. Chem. Phys.*, **72**, 2340 (1980).
73. J. R. Durig, R. O. Carter, and L. A. Carreira, *J. Chem. Phys.*, **60**, 3098 (1974).

74. Y. Inoue, T. Ueoka, T. Kuroda, and T. Hakushi, *J. Chem. Soc. Chem. Commun.*, 1031 (1981).
75. A. C. Cope and B. A. Pawson, *J. Am. Chem. Soc.*, **87**, 3649 (1965).
76. D. W. Rogers, H. von Voithenberg, and N. L. Allinger, *J. Org Chem.*, **43**, 360 (1978).
77. J. Laane and R. C. Lord, *J. Mol. Spectr.*, **39**, 340 (1971).
78. Gaussian92/DFT, Revision F.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1993.